A thermal lens study of undoped and Fe₂O₃-doped silicate glasses at different wavelengths

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Abstract: The mode mismatched thermal lens technique has been used to determine the temperature coefficient of optical path length, ds/dT , of undoped and 2% Fe₂O₃-doped silicate glasses, at different wavelengths. The aberrant model, which takes into account the thickness change of the sample, was used as the theoretical model. The results showed that ds/dT is $(2.1 \pm 0.1) \times 10^{-6} \text{ K}^{-1}$ at 632.8 nm and $(2.4 \pm 0.1) \times 10^{-6} \text{ K}^{-1}$ at 442 nm for the undoped sample and $(4.66 \pm 0.03) \times 10^{-6} \text{ K}^{-1}$ at 632.8 nm and $(6.1 \pm 0.1) \times 10^{-6} \text{ K}^{-1}$ at 442 nm for the iron doped sample. The greater value of this parameter found for the doped sample at the Fe³⁺ absorption band (442 nm), was associated with the bigger value of the temperature coefficient of the electronic polarizability caused by the presence and environment of Fe³⁺ iron in the structure of the glass.

1. INTRODUCTION

CW mode mismatched thermal lens spectrometry (TLS) has been shown to be the most sensitive configuration for thermal lens techniques and has been applied successfully to study transparent materials[1,2]. The thermal lens effect is created when the excitation laser beam passes through the sample and absorbed energy is converted into heat. The consequent change in the optical path length induced by a temperature rise will produce a lens-like optical element at the sample, the so-called thermal lens. The propagation of a probe beam through the TL will be affected resulting in a spreading or focusing of the beam centre. By measuring its beam centre intensity variation in the far field, optothermal properties of the sample can be determined. The theoretical aberrant model treats the TL as an optical path length change to the probe laser beam, which can be expressed as an additional phase shift on its wave front after it passed through the sample[2-4]. This model is more accurate than the parabolic treatment in describing the behaviour of the thermal lens quantitatively, and one of the parameters determined from the experimental data is the temperature coefficient of optical path length in the sample, ds/dT .

There has been a great interest in the determination of ds/dT of technological glasses as it is associated with the nonlinear optical properties of the glass and is important when designing optical systems[5].

In this study the aberrant model of CW mode mismatched TLS spectrometry is applied to determine ds/dT of two samples of silicate glasses, one of them doped with 2% of Fe₂O₃. In the doped sample, the Fe³⁺ ion produces absorption bands around 440nm. Since in the mode mismatched TL configuration, ds/dT is associated to the probe beam wavelength, the experiments were performed with

probe beam at 442nm and at 632.8nm, by using steady state(SS) and time resolved(TR) measurements. The excitation beam was a Kr⁺ laser at 647.1nm, the sample preparation and TL experimental set up are described elsewhere[1,4].

2.RESULTS AND DISCUSSION

In the mode mismatched thermal lens spectrometry the probe beam intensity at the detector can be written as[2,3]:

$$I(t) = I(0) \left\{ 1 - \frac{\theta}{2} \tan^{-1} \left[\frac{2 m v}{[(1 + 2m)^2 + v^2] \frac{t_c}{2t} + 1 + 2m + v^2} \right] \right\}^2 \quad (1)$$

where

$$m = \left(\frac{\omega_{1p}}{\omega_e} \right)^2, \quad v = \frac{Z_1}{Z_c} \quad \text{when } Z_c < Z_2, \quad \theta = - \frac{P_e A_e I_0}{K \lambda_p} \frac{ds}{dT} \quad (2)$$

Here, t_c is the characteristic thermal time constant, ω_e excitation laser beam radius at the sample, K is thermal conductivity ($J s^{-1} cm^{-1} K^{-1}$), P_e is excitation laser beam power (mW), A_e is the optical absorption coefficient at the excitation beam wavelength (cm^{-1}), Z_c is the confocal distance of the probe beam, Z_1 is the distance between probe beam waist and sample, Z_2 is the distance between the sample and the detector, ω_{1p} is probe beam radius at the sample, θ is approximately the phase difference of the probe beam at $r = 0$ and $r = \sqrt{2}\omega_e$ induced by the thermal lens, λ_p is the probe beam wavelength and $I(0)$ is the value of $I(t)$ when t or θ is zero. Therefore, by measuring the probe beam intensity variation at the detector plane, ds/dT can be determined.

Figure 1 shows a normalised TR thermal lens signal for the doped sample, where the excitation beam power is 33.1mW and the probe beam at 632.8nm. At this wavelength, the experiments were done at seven different excitation laser beam powers, and from the θ value at each power and by using Eq. 2(for θ) ds/dT were obtained as: $(4.66 \pm 0.03) \times 10^{-6} K^{-1}$ for the TR and $(4.63 \pm 0.06) \times 10^{-6} K^{-1}$ for the SS measurements, shown in Figure 2. There was no significant difference between the two methods, therefore we present only TR results for ds/dT in the table I.

Table I. Time Resolved Results for ds/dT at 442 nm and at 632.8 nm

Sample	$\times 10^{-6} K^{-1}$ (442 nm)	$\times 10^{-6} K^{-1}$ (632.8 nm)
Doped	6.1 ± 0.1	4.66 ± 0.03
Undoped	2.4 ± 0.1	2.1 ± 0.1

Our results for ds/dT can be discussed using the following equation for glasses[2,5-7]:

$$\frac{ds}{dT} = (n_0 - 1) (1 + v) \alpha + \frac{(n_0^2 - 1) (n_0^2 + 2)}{6 n_0} (\phi - \beta) \quad (3)$$

where, n_0 is the initial refractive index at the initial temperature T_0 , α is the linear temperature coefficient of thermal expansion, and ϕ and β are the temperature coefficient of electronic polarizability and volume expansion respectively and ν is the Poisson ratio. The first term of Eq. 3 comes from sample thickness change and its time response is supposed to be longer than the μs scale. Our experiments were carried out in the ms scale and steady state measurements, therefore this term is likely to contribute to ds/dT results shown in table I. The second term in Eq. 3 is the refractive index change with temperature rise and is obtained from the Lorentz-Lorenz relation(8). It can be seen that ds/dT is mainly controlled by β and ϕ values.

The contribution of each term to ds/dT depends on the structure and composition of the sample. For glasses, ϕ has been associated with the electronic polarizing power(Z/a^2) of the network forming ions[7], where a decrease in the ratio, Z/a^2 , produces an increase in the ϕ value of the polarizable ions linked to the structure former.

For the doped sample, the thermal lens is dependent on both intrinsic and extrinsic optical absorption. The latter is dependent on the presence and environment of Fe^{3+} ion in the sample. In a previous study it has been demonstrated that Fe^{3+} ions are the predominant oxidation state in this sample and that these ions are mainly in a network forming position, occupying sites similar to the silicon ions in the sample[9].

Therefore, considering that the excitation beam is the same and only the probe beam is changed to measure ds/dT at different wavelengths, the higher value of this parameter at 442nm for the undoped sample can be associated to the higher value of the electronic polarizability at that wavelength. The effect of the refractive index change between these wavelengths for ds/dT is very small and can be negligible. The difference between ds/dT at 442 nm and 632.8 nm was more pronounced for the doped sample. In

Figure 1. Time resolved experimental data and their best fit curve for the doped sample. The power of excitation beam is 33.1 mW at 647.1 nm; the probe beam is at 632.8 nm.

Figure 2. Experimental data and their best fit curves versus different excitation laser powers at 647.1 nm for doped sample: (a) time resolved, (b) steady state. Probe beam is at 632.8 nm.

this case, the sample presents an absorption band at 442 nm due the presence and environment of the Fe^{3+} ions. Therefore, considering that the electronic polarizability becomes bigger near to the absorption band, the greater difference in ds/dT observed can also be associated to the higher value of the electronic polarizability of the sample at 442 nm, induced by Fe^{3+} ion environment in the sample.

In conclusion, this work has shown the application of the aberrant model to mode mismatched TLS to determine ds/dT of silicate glasses at 442nm and 632.8nm. It was found that the higher value of ds/dT at 442nm can be associated to the higher value of the electronic polarizability induced by the presence of Fe^{3+} in the doped sample. Furthermore, the more realistic theoretical treatment of the TL by the aberrant model, where the whole optical path length change is taken into account to determine ds/dT quantitatively at room temperature, make the technique useful to study optothermal properties of glasses.

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